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Annual Report on "Liquid Crystalline 3d Porphyrin Complexes," 7/1/85-6/30/86

The goals of this project are to prepare novel materials composed of transition metal porphyrin derivatives linked in polymeric form through bidentate bridging ligands such as oxide, cyanide or pyrazine. Such materials are expected to manifest unusual collective solid state properties, especially electrical conductivity, optical absorption in the far-infrared, and intrachain magnetic interactions. Since the 4d and 5d metal derivatives have been discovered to manifest stronger interactions, these have been included in this study. Initial work has focused on simple porphyrins, but the free base liquid crystalline "mesodiscotic" phthalocyanines have been prepared and we intend to study them in the later phase of this project.

We have now prepared several members of a family of polymeric iron, ruthenium and osmium polymers which are linked by pyrazine, cyanogen, and cyanide bridges. Oxidatively doped members of this family exhibit semiconductivity. Their conductivities are mirrored by optical absorption in the near infrared. These conductivities and "intervalence absorption spectra" follow the trend osmium > ruthenium >> iron. Oxidative doping has been accomplished both chemically and electrochemically. We have utilized a new carbon cloth electrode method for the latter. Conductivity is a function of the extent of oxidation and reaches a maximum at about 0.3 electrons per metal atom.

Two papers have been published as a result of this work. Reprints have been sent under separate cover. This research has involved two physicists, W.A. Little (Stanford) and J. Torrance (IBM San Jose) as well as a crystallographer J. Ibers (Northwestern University).

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